THE KINETICS OF OXIDATION-REDUCTION OF VANADIUM
IONS ON VARIOUS ELECTRODES

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16. Abstract

The existence of inhibited phases preceding the phase of electron transfer in the oxidation-reduction of vanadium ions on various electrodes was examined. The experimental conditions are described in detail.

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IONS ON VARIOUS ELECTRODES

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According to [1], in sulfate solutions with pH from 0 to 2, there are mainly such forms of vanadium as VO_2^+, VO^{2+}, and V^{3+} (the ccordination of SO_4^{2-} ions is more weakly expressed than oxygen and is therefore not considered).

Previously [2-3] the authors established that the diffusion equations which describe the oxidation-reduction of vanadium ions on various electrodes contain stoichiometeric coefficients of chemical interaction which differ from one another.

It was of interest to make certain of the existence of inhibited phases preceding the phase of electron transfer, and of the individuality of the limiting currents observed in the given system. For this purpose we used the methods of voltamperometry to study such functions as: the non-stationary outputs with respect to the current of vanadium ions with currents less than the limiting current; the dependence of the limiting currents on the potential development time and the concentration of vanadium; the effect of mixing, pH and the content of SO_4^{2-} ions on the electrochemical parameters of the polarization curves.

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* Numbers in margin indicate pagination in original foreign text.

The current-potential curves were made by means of the potentiostat P-5827 and recorded by the millimeter M-253 and the electron potentiometer KSP-4. The working solutions were prepared from vanadium sulfate $VOSO_4 \cdot 3H_2O$ ("analytically pure") and ammonium m-vanadate—NH_4VO_3 ("analytically pure"), acidified with sulfuric acid to the required pH. When necessary, the solutions of VO_2^+ were obtained by anaodic oxidation of vanadium sulfate. The content of vanadium ions was determined by volumetric titration with respect to an indicator or amperometrically — directly in the electrochemical cell. For extraction we used electrodes of platinum, palladium, rhodium, lead, copper and iron in the form of plates with a surface of 1 cm^2, sealed in a glass tube. The electrodes were polished with diamond paste, degreased with French chalk and alcohol, secured and washed off. Beforehand, the electrodes were switched on briefly in order to bring them to a stationary condition. The greater part of the experiments was carried out with solutions containing 10 g/l V (+4).

In Figure 1 we present the relationship of the limiting current of vanadium to the concentration of VO^{2+} ions during anodic oxidation with rhodium. Analogous results were obtained with a platinum anode, and with copper and iron cathodes. The magnitudes of the limiting currents rose sharply with the intensity of stirring.

/584

In Figure 2, the dependence of the non-stationary limiting currents on time is presented. The slopes of the coefficients of the straight lines 1, 2, 3 and 4, 5 , 6, containing the constants of the diffusion current behave in the first approximation like prime numbers — 1:2. This result is in agreement with the data from [2,3], and obviously is connected with the difference in chemical states in various electrodes, and accordingly, in the stoichiometric coefficients.

2

TABLE 1. EFFECT OF SO_4^{2-} ION CONCENTRATION ON THE
HEIGHT OF NON-STATIONARY LIMITING CURRENTS

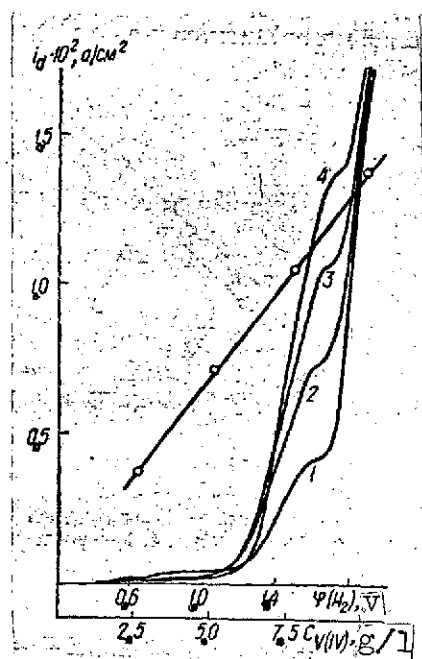| Electrode	Added Sulfate, g/l	i_d, a/dm^2
Pt anode	–	1.5
	8	1.6
	27	1.5
Cu cathode	–	2.5
	8	2.6
	27	2.5

Figure 1.   The effect of the VO^{2+} concentration on height
i_d(Rh-anose $VOSO_4$); 1-2.5, 2-5.0, 3-7.5, 4-10 g/l V(+4).

During anodic oxidation of VO^{2+} on platinum, rhodium and palladium, the limiting currents have approximately the same value (Table 2) despite the enormous difference in output of VO_2^+.

In sulfate solutions the formation of complexes of ions of vanadium with oxygen, SO_4^{2-} ions and molecules of water is possible. To clarify the role of ionic interaction in the kinetics of the redox-processes, we studied the effect of concentration of SO_4^{2-} ions on the magnitudes of the limiting currents, and also the effect of pH on the speed of the process in the presence of a constant potential. These results are presented in Table 1 and Figure 3. The height of the limiting current does not depend on the sulfate content, but its occurrence cannot possibly be connected with slowing down of ionic interaction prior to discharge (Table 1).
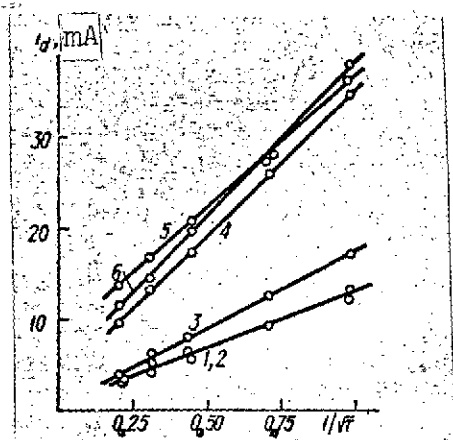

Figure 2. Dependence of i_d on the speed of removal: 1,2,3— oxidation of VO^{2+} to VO_{2+} on Pd, Rh, Pt; 4,5,6 — reduction of VO_{2+} to VO^{2+} on Fe, Pb, Cu.
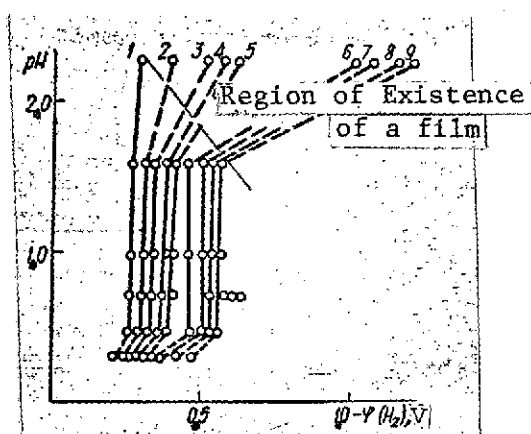

Figure 3. The relationship φ–pH in a solution of $VOSO_4$ on a copper cathode at currents from 1.25 (1) to 62.5 mA (9).

TABLE 2.   NON-STATIONARY OUTPUTS WITH RESPECT TO CURRENT IN A
SOLUTION WITH CONCENTRATION V(+4), EQUAL TO 10 g/l, AND pH 70

Anode outputs with respect to current			i_d, mA/cm^2	Cathode outputs with respect to current		
Anode material	$\varphi(H_2)$, v	η,%		Cathode material	$\varphi(H_2)$,v	η,%
Pd	+1.58	6.9	13.5	Pd	-0.60	7.1
Pt	+1.52	94.0	17.0	Cu	-0.34	21.0
Rh	+1.70	55.0	14.0	Pb	-040	67.5

In the working pH interval from 0.3 to 1.5, the speed of
reaction is practically unchanged. For pH 2 or higher, the polari-
zation increased sharply, and on the surface of the anodes and
cathodes oxide films were formed. When the pH was less than 0.3,
some depolarization was observed, connected, possibly, with the
change in coordination of oxygen.

The outputs with respect to the current were determined with
current densities which were lower than the limiting currents in
non-stationary conditions. In order to avoid a transition of the
system to current densities higher than the limiting ones and a
change of the mechanism of the process, the outputs with respect to
the current were measured when the potential was constant. The
amount of electricity was determined by graphical integration of
the current-time curve, and the change in concentration of VO^{2+}
ions — by amperometric titration directly in the cell. The re-
sults obtained are presented in Table 2. In all the experiments,
the outputs with respect to the current differed from 100%. On
the platinum cathode on which only one branch of the polarized
curve was observed, the output with respect to the current did not

attain 100%, even when the polarizations were very small [3]. These data are hard to explain if one considers the discharge of the ions of VO^{2+} and H_2O as independent.

Thus, although the electrochemical behavior of the systems studied meets the criteria which are ordinarily considered sufficient for recognizing the limiting currents as diffusional — their nature is more complex. Obviously a detailed interpretation of the kinetic data must account for the conjugacy of the redox-reaction of vanadium ions with the processes of separation of hydrogen and oxygen and the rapid chemical interaction of the products of the reaction.

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6